

RECEIVED 12 JUL 2004

P1 1189838

<u> TO AIL, TO WHOM THESE: PRESENIS SHAIL COME:</u>

UNITED STATES DEPARTMENT OF COMMERCE **United States Patent and Trademark Office** 

July 06, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/467,212

FILING DATE: May 01, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/13413

By Authority of the

COMMISSIONER OF PATENTS AND TRADEMARKS

M. SIAS

**Certifying Officer** 

**PRIORITY** 

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)



## 05-01-0501457212.0501

Please type a plus sign (+) Inside this box +	PTO/SB/16 (8-0) Approved for use through 10/31/2002. OMB 0651-003 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCI
no Processory Reduction Act of 1995, no persons are required to respond t	o a collection of information unless it displays a valid OMB control number.

PROVISIONAL APPLICATION FOR PATENT COVER SHEET This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

•	INV	ENTOR(S	)			
1 110 75 1	Family Name or	Sumama	Residence (City and either State or Foreign Country)		四重	
Given Name (first and middle [if any])  Chuck	Marino	Odmanio	Philadelphia, Pennsylvania USA			
Reynolds	Kim		Berwyn, Pennsylva	nia USA		2.012
•		•			<u> </u>	
Additional inventors are being nam	ed on tht separat	tely number	ed sheets attached he	reto		
,	TITLE OF THE INVE	ENTION (28	0 characters max)			* - = =
THERMALLY CONDUCTIVE FLUOROCA	RBON POLYMER CO	OMPOSITE				
Direct all correspondence to:	CORRESPO	NDENCE A	ADDRESS			—, <u>l</u>
Customer Number					ce Customer Number Code Label here	
OR Type C	ıstomer Number here					
	estvedt & Lechner LL					
Individual Name ,	Aramark Tower					
Address	Market Street			,		
Address	delphia i.	State	PA	ZIP	19107-2950	
City USA		Telephone	(215) 923-4466	Fax	(215) 923-2189	
EN	ICLOSED APPLICAT		6 (check all that appl	y)(y		
Specification Number of Pages	12		CD(s), Number			
Drawing(s) Number of Sheets			Other (specify)	[		
Application Data Sheet. See 37 C	FR 1.76		Utiler (specify)	<u></u>		
METHOD OF PAYMENT OF FILING F		VISIONAL	APPLICATION FOR P	ATENT (	check one)	
WETTOD OF THE STATE OF THE STATE OF					FILING FEE AMOUNT (\$)	1
A check or money order is end	dosed to cover the filling	ng fees			AWOONT	· ·
The Commissioner is hereby a fees or credit any overpaymen	uthorized to charge file	ling Number	19-5425		\$160.00	
Payment by credit card. Form	PTO-2038 is attached	<b>i</b> .'				
The invention was made by an agency	of the United States	Governmen	it or under a contract w	vith an ag	jency of the	
United States Government.	•					1
Yes, the name of the U.S. Government	agency and the Govern	nent contract	number are:			l l
Respectfully submitted,			Date	5-1-03	لنـ	
SIGNATURE	_			TRATIO	N NO. 32,29	0
TYPED or PRINTED NAME Joseph I	Posillico	•		<i>ropriate)</i> t Numbe	P-26,190	USA
	3-4466					

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any gathering, preparing, and submitting the complete this form and/or suggestions for reducing this burden, should be sent to the Chief comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief formation Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR Information Officer, U.S. Patent and Trademark Office, U.S. Popartment of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR Information Officer, U.S. Patent and Trademark Office, U.S. Popartment of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR Information Officer, U.S. Patent and Trademark Office, U.S. Popartment of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR Information Officer, U.S. Patent and Trademark Office, U.S. Popartment of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR Information Officer, U.S. Patent and Trademark Office, U.S. Patent and Trademark Office

-1-

PATENT Attorney Docket No. P-26,190 USA Express Mail Label No. EV 262353184 US

## THERMALLY CONDUCTIVE FLUOROCARBON POLYMER COMPOSITE

## FIELD OF THE INVENTION

The present invention relates to thermally conductive polymer composite materials, conductive members and surfaces containing such materials, to heat exchange equipment containing such members and surfaces, and to methods of making each of these.

## BACKGROUND OF THE INVENTION

Numerous applications require the transfer of heat across or through a thickness of solid material. For example, home heating systems typically conduct heat from hot air or water through the wall of the conduit or duct which contains the hot fluid. Other applications which require such a transfer of heat include automotive heater cores, radiators, evaporators, condensers, charge air coolers, and transmission/engine oil coolers. Such devices, and many others that operate on the same principle, are typically referred to as heat exchange devices. Heat exchange devices play a critical role in many industrial applications, especially in the chemical, petroleum and power industries.

The material which forms the wall through which heat flows in such devices most desirably has a high degree of thermal conductivity. Thermally conductive metals, such as aluminum, copper and frequently more exotic metals and alloys, have heretofore been frequently used for their desirable combination of strength and good thermal conductivity. However, such materials do not always possess the best overall combinations of properties for particular applications. For example, in many applications in the chemical industry the heat exchange surface must be in contact with highly corrosive chemicals. Metals which are adequate in such environments are often detrimentally expensive. The

Express Mail Label No. EV 262353184 US

requirement of good thermal conductivity and excellent resistance to corrosion is also present in certain battery applications, as disclosed for example in U.S. Patent No. 5,786,107, which is incorporated herein by reference.

In other applications, the metallic products which have heretofore been used are not easily formed into the shape required by certain heat exchange devices. For example, many heat exchange devices require the use of tubes with fins or similar projections in order to increase the heat transfer surface. Forming such an arrangement from metals is frequently difficult, time consuming and expensive. Furthermore, there has been a trend in the industry to form such devices with very thin fins, and this trend has caused a variety of problems for heat exchange equipment in which the heat transfer surfaces are formed from metallic materials, as noted in U.S. Patent No. 6,329,075.

Advances in the electronics industry has also created a need for improved heat conducting materials. As electronic components, especially computers and similar devices which rely on microprocessors, operate at faster and faster speeds and become smaller and smaller, the problem of managing the heat generated by such devices becomes critical. For instance, heat build-up in electronic products leads to reduced reliability ("mean-time-to-failure"), slower performance, and reduced power-handling capabilities. In addition, continued interest in increasing the number of electronic components on, and reducing the size of, semiconductor chips, notwithstanding the desire generally to reduce power consumption thereof, also contributes to the importance of thermal management. Also, chip-on-board technology, where semiconductor chips are mounted directly to printed circuit boards, creates further demands on thermal management because of the more efficient use of surface area thereon.

Thermal management techniques include generally convection and/or conduction mechanisms, where heat may be removed from electronic devices (such as operating silicon integrated circuits) by air (e.g., free flowing or forced) convection around the device, fluid (e.g., water or other fluid) convection through radiators, evaporators, reactors and the like, or conduction through the solid parts of the heat

-3-

PATENT Attorney Docket No. P-26,190 USA Express Mail Label No. EV 262353184 US

exchange equipment which are in contact with the fluids and through which the heat must flow. A combination of such techniques is often used to maintain temperatures within design criteria.

Heat conduction, which is the more important phenomenon for the present invention, involves heat flow per unit area over a length which is proportional to the temperature gradient across that length. Thus, heat conduction (or thermal conductivity) is a steady-state property measuring the ability of a certain material to transfer heat there through.

The present inventors have discovered a highly desirable and advantageous polymer-based material which is especially well adapted for use as or in connection with heat transfer equipment, which has a high degree of thermal conductivity, which is readily formable into a wide variety of shapes, which has excellent corrosion resistance, and which is cost effective relative to certain heretofor used metal-based material.

## SUMMARY OF THE INVENTION

The present inventors have discovered that many of the above noted difficulties are overcome by a polymer composite comprising a major proportion of fluorocarbon polymer and a minor proportion of boron nitride. As used herein the terms "boron nitride" and "B(N)" to refer to is used herein to mean and identify all phases and compounds consisting essentially of boron and nitrogen. The notation "B(N)" as used herein thus indicates that some or all of nitrogen may be bound (covalently and/or ionically) to the boron, such as in BN, but is not limited to this compound. Thus, the notation "B(N)" also covers the stoichiometry BN<sub>2</sub>, BN<sub>3</sub> and other effective and possible stoichiometries and/or combinations of boron and nitrogen.

4-

PATENT Attorney Docket No. P-26,190 USA Express Mail Label No. EV 262353184 US

## DETAILED DESCRIPTION

The polymer composite of the present invention comprises a major proportion by weight of resin of fluorocarbon polymer and from about 2 % to about 40 % by weight of B(N), more preferably from about 2 % to about 20 % by weight of B(N) and even more preferably from about 5 % to about 15 % of BN. Applicant believes that a critical range exists in the amount of B(N) used in the thermally conductive polymer composite of the present inventions. This criticality is based on the need for the composite to at once have a difficult to achieve combination of properties. More particularly, the amount of the B(N) should be effective to substantially improve the thermal conductivity of the fluorocarbon polymer, which would otherwise be a very poor thermal conductor. At the same time, the amount of B(N), and in certain embodiments the type and nature of the B(N), should not have a deleterious effect on the mechanical strength and stability of the composite or on the ready formability of the composite. For example when the fluorocarbon polymer comprises PTFE, the preferred ranges specified herein provide ready extrudability by paste extrusion while at the same time achieving the desirable thermal and mechanical properties described above. Similarly for melt extrudable fluorocarbon polymers, such as FEP and PFA, the preferred ranges specified herein provide adequate melt strength while at the same time achieving the desirable thermal and mechanical properties in the finished product.

As the term is used herein, fluorocarbon polymer refers to and is intended to include not only a single fluorocarbon polymer entity but also a mixture of any two or more fluorocarbon polymer entities. As is well known, fluorocarbon polymers are a class of paraffinic polymers which have some or all of the hydrogen replaced by fluorine. It is contemplated that the present composites can be formed from any one of these polymeric components. The fluorocarbon polymer component of the present composite is preferably selected from group consisting of polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP), perfluoroalkoxy (PFA) resin, polychlorotrifluoroethylene (PCTFE), ethylenetrichlorotrifluoroethylene copolymer (ETFE),

Express Mail Label No. EV 262353184 US

polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), copolymers and terpolymers including any one or more of these, and mixtures of two or more of these. While it is contemplated that all of the above fluorocarbon polymers, including homopolymers, copolymers, block and graft copolymers of any of the above, may be used, PTFE, PFA and FEP are preferred.

Is contemplated that numerous types and varieties of B(N) may be used effectively in accordance with the present invention, and all such types and varieties are within the scope hereof. In certain preferred embodiments, the boron nitride used in the compositions of the present invention is in the form of a powder comprised of particles having a hexagonical crystal structure and large, graphite like platelets. Such a powder is available from Advanced Ceramics Corp. of Cleveland OH under the trade designation "Boron Nitride Powder - Grade AC – 6004." A copy of a product sheet describing the particular characteristics of this powder is attached hereto and incorporated herein by reference.

According to preferred aspects of the present invention which utilize fluorocarbon polymer resins that are paste extrudable, such as PTFE, such resins are generally in the form of extrusion grade powders, fine powders, and the like. For embodiments in which the polymeric component is PTFE, it is preferred that the PTFE powders are dispersion grade and not granular. Techniques for the production of fine PTFE powders are well known, and the use of polymers produced by any of these techniques is well within the scope of this invention. For example, fine PTFE powder may be produced by coagulating colloidal PTFE particles as disclosed in U.S. Pat. No. 4,451,616, which is incorporated herein by reference.

For resins that are melt extrudable, it is contemplated that a wide variety of conditions and process parameters can be used within the scope of the present invention. In certain embodiments, it is preferred that extrusion temperature ranges from about 500 to about 800°F, more preferably about 550-

Express Mail Label No. EV 262353184 US

700°F., with the screw revolutions per minute (RPM) ranging from about 1 to about 100 RPM, more preferably 5-50 RPM.

Although it is contemplated that the amount of fluorocarbon polymer used in the present composite can vary widely within the scope of the present invention, it is generally preferred that the composite comprise at least about 60% by weight of fluorocarbon polymer, more preferably at least about 75% by weight of fluorocarbon polymer, and even more preferably at least about 85% by weight of fluorocarbon polymer.

In preferred embodiments, the present composite is a formed composite, such as a film, plate, tubular member, finned tubular member and the like, having a thermal conductivity which is at least 50%, and even more preferably at least about 100% greater than the thermal conductivity of the same formed product made from the fluorocarbon polymer alone. In preferred embodiments, the present invention provides formed composites having a thermal conductivity, Tc, of at least about 1.5 (W/m/K), more preferably at least to about 2 (W/m/K) and even more preferably at least to about 2.5 (W/m/K). As will be appreciated by those skilled in the art, these values compare very favorably to the value, for example, of neat FEP resin, which has a thermal conductivity of about 1.1(W/m/K). In highly preferred embodiments, the formed composite has a thermal conductivity of at least about 3 (W/m/K).

The present composites may optionally include other fillers (both organic and inorganic), lubricants, pigments and other modificants as will be appreciated by those skilled in the art.

The composites of the present invention can be formed by a wide variety and combination of techniques in view of the teachings contained herein, and all such methods are within the broad scope of the present invention. In preferred embodiments, however, the composite is formed by intimate mixing of the fluorocarbon polymer and the B(N) under conditions effective to achieve a substantially

Express Mail Label No. EV 262353184 US

homogeneous mixture of thereof. One preferred method for formulating such composites comprises mixing the polymer resin, and preferably fluorocarbon polymer in the form of fine powders, with particulate B(N) Another method is co-coagulation of the resin and the B(N). Any well known mixing process that achieves homogeneous and uniform mixing may be employed, although for paste extrusion techniques mixing by tumbling in a suitable commercial blender such as a Patterson Kelly Twin Shell at temperatures up to about 68.degree. F. for a period of about 3 minutes is generally preferred. For melt processes, it is expected that twin screw type mixing techniques are commonly used, but all other applicable techniques are also within the scope of the present invention.

The heat exchange structures of the present invention can be formed by a wide variety and combination of techniques in view of the teachings contained herein, and all such methods are within the broad scope of the present invention. In preferred embodiments, however, the particles of B(N) are blended with the fluoropolymer in amounts sufficient to attain a composite that is at once readily extrudable (most preferably by paste extrusion in the case of PTFE), has a relatively high structural integrity, and has a thermal conductivity in accordance with the present invention. In general, it is preferred according to the present invention that the shaped composites of the present invention are produced by paste extrusion. In the paste extrusion process, the fluorocarbon polymer, the B(N) and any other modificants which may be present, are integrated into a substantially homogeneous mass and then compressed into the appropriate pre-formed shape, preferably a cylindrical shape, by techniques well known in the art. An extrusion aid, such as naphtha or other volatile paraffinic hydrocarbon, may be added to the pre-formed composite in an amount of from about 15% to about 20% by weight. The preformed composite is then shaped into the desired form by cold flow extrusion according to techniques well known in the art.

Express Mail Label No. EV 262353184 US

After extrusion, the extrusion aid is substantially removed from the shaped article. According to one embodiment, removal of the extrusion aid comprises heating the shaped composite for time and at a temperature sufficient to effect removal of the extrusion aid, typically for about 15 seconds at about 350°F. The shaping process further preferably comprises a sintering step in which the extruded composite is heated for time and at a temperature sufficient to fuse or sinter the compressed powders into a homogeneous product, typically for about 20 seconds at about a temperature of at least about 647°F. (342°C.). The shaping process may be, and preferably is, carried out continuously.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention.

Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

Express Mail Label No. EV 262353184 US

#### What is claimed is:

- A thermally conductive heat exchange structure comprising a polymer composite comprising a
  major proportion of fluorocarbon polymer and a minor proportion of boron nitride.
- The thermally conductive heat exchange structure of claim 1 wherein said polymer composite comprises from about 2 % to about 40 % by weight of B(N).
- 3. The thermally conductive heat exchange structure of claim 1 wherein said polymer composite comprises from about 5 % to about 15 % of BN.
- 4. The thermally conductive heat exchange structure of claim 2 wherein said polymer composite comprises at least about 60% by weight of fluorocarbon polymer.
- The thermally conductive heat exchange structure of claim 2 wherein said polymer composite comprises at least about 75% by weight of fluorocarbon polymer.
- The thermally conductive heat exchange structure of claim 2 wherein said polymer composite comprises at least about 85% by weight of fluorocarbon polymer.
- The thermally conductive heat exchange structure of claim 2 wherein said polymer composite comprises from about 85% to about 98% by weight of fluorocarbon polymer.
- 8. The thermally conductive heat exchange structure of claim 1 wherein said polymer composite has a thermal conductivity of at least about 1.5 (W/m/K).
- 9. The thermally conductive heat exchange structure of claim 1 wherein said polymer composite has a thermal conductivity of at least to about 2 (W/m/K).
- 10. The thermally conductive heat exchange structure of claim 1 wherein said polymer composite has a thermal conductivity of at least to about 2.5 (W/m/K).
  - 11. The thermally conductive heat exchange structure of claim 1 wherein said polymer composite comprises from about 2 % to about 20 % by weight of B(N).

-10-

PATENT Attorney Docket No. P-26,190 USA Express Mail Label No. EV 262353184 US

## ABSTRACT OF THE DISCLOSURE

A thermally conductive heat exchange structure comprising a polymer composite comprising a major proportion of fluorocarbon polymer and a minor proportion of boron nitride.

M:\UPosillico\Markel Corporation\P-26,190 USA\ProvApp.wpd



**Boron Nitride Powder Grade AC-6004** 

Grade AC-6004 is a high purity, fine (99.9%, -325 mesh) Boron Nitride (BN) powder with a hexagonal crystal structure and large graphite-like platelets. It exhibits the UNIQUE properties of boron nitride in a form readily used in the production of many advanced materials.

A unique manufacturing process achieves larger size crystals (>10 $\mu$ ) with lower surface area (2.0 m<sup>1</sup>/g), compared to Grade HCP, which provides enhanced lubricity and thermal properties.

#### FOR USE IN:

The production of thermally conductive materials including adhesives, pastes, polting compounds and other polymer matrices.

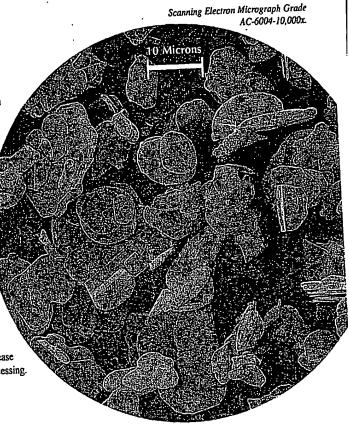
Also for use in electronic applications where a combination of excellent thermal conductivity and high electrical resistivity are desired.

Grade AC-6004 is also used as an ingredient in a variety of release agents and lubricants for high temperature metal and glass processing.

## GENERAL CHARACTERISTICS OF BORON NITRIDE

- · Electrical Insulator
- Low Dielectric Constant
- Low Dielectric Loss
- High Temperature Stability
- Thermal Conductor
- Lubricious
- · Inert
- · Non-Wetting

BN powders are produced by Advanced Ceramics Corporation in more than 70 individual grades to meet a wide range of application requirements.



**ISO 9002 CERTIFIED** 

# Advanced Ceramics Advanced Ceramics Corporation Very advanced, indeed.

Sales Office P.O. Box 94924 • Cteveland, Ohio USA 44101-4924 Phone: 800-822-4322 • E-Mail: info@advceramics.com

## Grade AC-6004

**Boron Nitride Powder** 

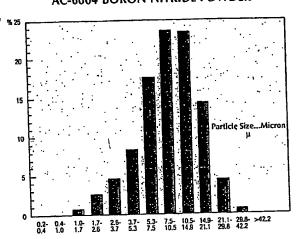
#### **TYPICAL PROPERTIES—GRADE AC-6004**

Crystal (type)	Hexagonal (Graphitic)
Color ·	White
Mean Particle Size	9 to 12μ
Crystal Size	>10µ
% -325 Mesh	99.9
Surface Area m²/g	2 .
Tap Density, g/cc	0.55
Oxygen, %	0.30
Sol. Borate, %	0.15
Carbon, %	0.02
Moisture, %	0.15

#### ELEMENTAL

•	
Cu, Al, Mg, K, Fe, Si, Ti	<100ppm, each element
Cl, S, F, Na	<20ppm, each element
Other Metals	<10ppm cach

## AC-6004 BORON NITRIDE POWDER



The information contained herein is, to the best of our knowledge, true and accurate. Data are typical and will vary within ranges established for a particular grade. These products are sold without warranty, either expressed or implied, of fitness for a particular purpose or use. All risks associated with the use of these products are assumed by the user.

www.advceramics.com

Rev. 10/01 2.5M

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Def	ects in the images include but are not limited to the items checked:
[	BLACK BORDERS
	IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
	☐ FADED TEXT OR DRAWING
	☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
	☐ SKEWED/SLANTED IMAGES
	COLOR OR BLACK AND WHITE PHOTOGRAPHS
	GRAY SCALE DOCUMENTS
	LINES OR MARKS ON ORIGINAL DOCUMENT
	REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

## IMAGES ARE BEST AVAILABLE COPY.

☐ OTHER:

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.